# Use of JANAF Tables in Equilibrium Calculations and Partition Function Calculations for an Undergraduate Physical Chemistry Course

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ABSTRACT: The usefulness of the JANAF tables is demonstrated with specific equilibrium calculations. An emphasis is placed on the nature of standard chemical potential calculations. Also, the use of the JANAF tables for calculating partition functions is examined. In the partition function calculations, the importance of the zero of energy is highlighted.

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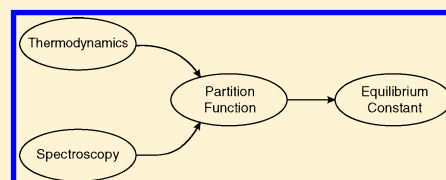
A typical undergraduate physical chemistry curriculum will focus considerable attention on thermodynamics and quantum mechanics. In the thermodynamics coverage, the chemical potential is introduced and shown to be of primary importance when developing a quantitative picture of equilibrium, be it physical or chemical equilibrium. What is not typically developed is how *numerical* values of these chemical potentials are determined. Moreover, it is not made explicit that numerical values of the chemical potential are based on a convention. If the convention changes, so too will the numerical values of the chemical potentials.

After enough thermodynamics and quantum mechanics have been covered, statistical mechanics is often introduced. Just as the chemical potential holds center stage in thermodynamics, the partition function is the key to statistical mechanics. Partition functions allow thermodynamic parameters to be determined from quantum mechanical energy levels. Given that thermodynamic parameters can be determined from partition functions, it should be possible to recover a partition function value knowing only the thermodynamic parameters.

Thermodynamic parameters such as heat capacity and entropy can be found in the Joint Army-Navy-Air Force (JANAF) tables. These tables were first distributed in 1960.[1] They were produced in response to a need for validating thermodynamic calculations. Specifically, calculations were being performed on solid propellants in the 1950s that needed validation. Hence the military interest in the development of what became the JANAF tables. They continue to this day having regular updates in the form of supplements. The JANAF tables are but one of many sources for thermodynamic data. Jacobson provides information on more than a dozen such sources.[2]

We have found that the introduction of JANAF tables into the undergraduate physical chemistry curriculum, following the lead of McQuarrie and Simon,[3] allows us to better develop the quantitative aspect of the chemical potential. In addition, introducing the JANAF tables has allowed us to provide a sense of internal consistency between quantum mechanics and thermodynamics when we demonstrate that partition functions can be calculated from thermodynamic parameters presented in JANAF tables.

Most tables in physical chemistry textbooks that provide enthalpies of formation or Gibbs free energies of formation do so only at 298.15 K. An additional advantage of introducing the use of JANAF tables in physical chemistry is that calculations are possible over a wide range of temperatures. Hence, trends such as the change in the enthalpy of a reaction with temperature can be examined and compared to general statements such as "...ΔH^0 and ΔS^0 for reactions not in solution change slowly with T...".[4]

Andersen reviewed the use of JANAF tables, and other sources, for the purpose of calculating the equilibrium constant and enthalpy of reaction at various temperatures.[5] In his work, he did not mention the standard chemical potential but rather focused on the heat capacity data.

A major part of undergraduate physical chemistry is equilibrium calculations. In the course of these calculations, values of the standard chemical potential, $\mu^0(T)$, are required. The standard chemical potential of component i is defined as

$$\mu_i^0 \equiv \frac{\partial G^0}{\partial n_i} \tag{1}$$

where G^0 is the standard Gibbs free energy of the system and n_i is the number of moles of component i in the system. The superscripts used here are consistent with acceptable chemical notation where the superscripts indicate *standard* conditions. For example, when working with gases, the standard conditions include the condition that the gases be treated as ideal gases. The standard chemical potential will have the units of energy/mol. There is always an emphasis in physical chemistry that energy values are reported relative to a value. Unlike volume,

for example, which can be reported absolutely, enthalpy (H) and the Gibbs free energy (G) are reported as relative to some value, hence the tabulated values of ΔH_f^0 and ΔG_f^0. In some physical chemistry texts values for $\mu^0(T)$ appear and are compared to accepted or literature values. It is not always clear how these literature values were determined. Moreover, the emphasis in energy calculations is that only differences in energy are observable, not absolute energies. So when a value such as $\mu^0(298.15) = -39.97$ kJ/mol for argon is reported (ref 3, page 948), it appears to contradict the assertion that only differences can be determined.

In this paper, we examine the use of the JANAF tables for the purpose of determining quantities such as $\mu^0(T)$. The use of these famous tables requires a bit of practice for an undergraduate chemistry student. Learning to use these tables also helps to cement the idea that energy values are indeed differences, namely, referenced to some value. Another attractive feature of facility with JANAF tables is the calculation of partition functions, q. While there is value in calculating partition functions from scratch using spectroscopic data, most calculations presented at the undergraduate level are limited in the degree of complexity of the model used to describe the system, namely, ideal gases. Since this is the standard state of a gas, it is appropriate for an equilibrium calculation involving gases where $\mu^0(T)$ is to be determined.

■ CALCULATION OF THE STANDARD CHEMICAL POTENTIAL

Argon Gas

We begin with a calculation of a standard chemical potential, $\mu^0(T)$, using the standard equations developed in statistical mechanics. For an atomic species with no rotational or vibrational contribution, the calculation reduces to a translational calculation, assuming the ground state of the atom is the zero of energy. The applicable equation from statistical mechanics is (ref 3, p 947)

$$\mu^0(T) = -RT \ln\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{kT}{P^0}\right] \quad (2)$$

where R is the universal gas constant, T is the temperature, m is the mass of the atom, k is Boltzmann's constant, h is Planck's constant, and P^0 is the standard pressure (1 bar). At 298.15 K, eq 2) gives a value of -39.97 kJ/mol for argon. To what should this value be compared? A quick scan of the JANAF table for argon at 298.15 K does not reveal any number close to -39.97 kJ/mol.[1,6] However, there are data in two columns which can be manipulated to produce $\mu^0(T)$. These are columns 4 and 5 with headings $-[G^0-H^0(T_r)]/T$ and $H^0-H^0(T_r)$. T_r is the *enthalpy reference temperature*, G^0 means $G^0(T)$, and H^0 means $H^0(T)$. The numerical value of T_r is identified at the top of the table. The calculation of $\mu^0(298.15)$ begins by multiplying column 4 by T/K (column 1) = 298.15 K, which produces 46,167.0 J/mol:

$$-[G^0 - H^0(T_r)]/T \times 298.15 = 46{,}167 \quad \text{J/mol} \quad (3)$$

where $T_r = 298.15$ K. Isolating G^0 gives

$$G^0(298.15) = -46{,}167.0 + H^0(298.15) \quad \text{J/mol} \quad (4)$$

This is where column 5 comes in. Column 5 gives the enthalpy at a temperature relative to the enthalpy at the reference temperature, T_r. Hence from column 5 at T/K = 0,

$$H^0(298.15) = H^0(0) + 6.197 \quad \text{kJ/mol} \quad (5)$$

The units in column 5 change to kJ/mol from J/mol in column 4. Equations 4 and 5 can be combined to give

$$G^0(298.15) = -46.167 + H^0(0) + 6.197 \quad \text{kJ/mol} \quad (6)$$

resulting in

$$G^0(298.15) - H^0(0) = \mu_{Ar}^0(298.15) = -39.97 \quad \text{kJ/mol} \quad (7)$$

The reason for referencing $G^0(298.15)$ to $H^0(0)$ lies in the definition of G, namely, $G = H - TS$. Hence, at 0 K, $G = H$. Therefore, $G^0(298.15) - H^0(0)$ could be replaced with $G^0(298.15) - G^0(0)$, which explicitly shows that G at temperature T is relative to G at 0 K.

This use of the JANAF tables in such a straightforward exercise accomplishes two goals. First, it provides a value to which a statistical mechanical calculation can be compared. Second, and more importantly, it shows explicitly that the value calculated in this example, -39.97 kJ/mol, is not an absolute value. It is a relative value. The notation in the JANAF table makes it clear that this value is relative to something, specifically the enthalpy or Gibbs free energy of argon at 0 K. If the standard chemical potential were reported relative to a different value, for example the reference temperature in the table, T_r,

$$G^0(298.15) - H^0(T_r) = -46.16 \quad \text{kJ/mol} \quad (8)$$

the standard chemical potential would decrease by 6.197 kJ, the value in column 5 at 0 K. Typically in the JANAF tables, the reference temperature is 298.15 K. It is explicitly stated on each table what reference temperature is being used.

Equilibrium Calculation

Next, we consider the need for standard chemical potentials at a given temperature for an equilibrium calculation. The ammonia equilibrium serves to illustrate several important features:

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g) \quad (9)$$
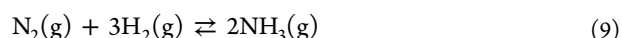
The standard Gibbs free energy change for this reaction is

$$\Delta G^0(T) = 2\mu_{NH_3}^0(T) - 3\mu_{H_2}^0(T) - \mu_{N_2}^0(T) \quad (10)$$

Using the above procedure involving columns 4 and 5, the three needed standard chemical potentials can be determined. The elements follow the above example. For example, to determine $\mu^0(T)$ for molecular hydrogen at 298.15 K,

$$-[G^0 - H^0(T_r)]/T \times 298.15 = 38{,}962 \quad \text{J/mol} \quad (11)$$

with the corresponding data from column 5,

$$H^0(298.15) = H^0(0) + 8.467 \quad \text{kJ/mol} \quad (12)$$

Combining these gives

$$G^0 - H^0(0) = \mu_{H_2}^0(298.15) = -30.50 \quad \text{kJ/mol} \quad (13)$$

A similar calculation for molecular nitrogen yields

$$G^0 - H^0(0) = \mu_{N_2}^0(298.15) = -48.46 \quad \text{kJ/mol} \quad (14)$$

Calculating $G^0 - H^0(0)$ for a molecular compound such as ammonia presents an additional layer of complexity. Naively applying the column 4 and 5 approach above will yield an energy value of -47.43 kJ (-86.34 kJ $- (-38.91)$ kJ, see Figure 1). Hence, the calculated value is referenced to the enthalpy at
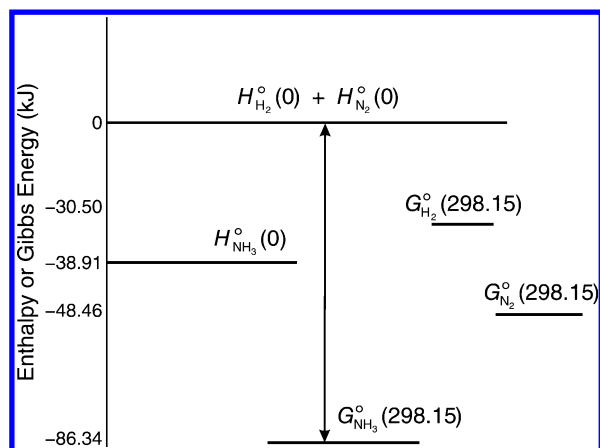
Figure 1. Values of $\mu^0(298.15) = G^0(298.15) - H^0(0)$ for H_2, N_2, and NH_3. The ammonia value must include the heat of formation of ammonia at 0 K (-38.91 kJ) in order that all three chemical potentials at 298.15 K are relative to the same energy level.

0 K of the *molecule*. In order to use the calculated standard Gibbs free energy of ammonia in a calculation involving hydrogen and nitrogen, all the standard Gibbs free energy calculations must be referenced to the same state. This is accomplished by adjusting the ammonia value so that it too is referenced to the elements. This is done using eq 15,

$$\mu^0_{NH_3} = G^0_{NH_3} - H^0_{NH_3}(T) + \Delta H^0_{f,NH_3,T} \tag{15}$$

and is shown by the double arrow in Figure 1. Equation 15 is applicable to the calculation of the standard Gibbs free energies of hydrogen and nitrogen, but in those calculations, the heat of formation values are zero. Applying this to ammonia at 298.15 K results in

$$-[G^0 - H^0(T_r)]/T \times 298.15 = 57{,}475 \quad J/mol \tag{16}$$

from column 4 and

$$H^0(298.15) = H^0(0) + 10.045 \quad kJ/mol \tag{17}$$

from column 5. These combine to give

$$G^0_{NH_3} - H^0_{NH_3}(0) = -47.43 \quad kJ/mol \tag{18}$$

Adjusting this for reference to the elements instead of ammonia (see JANAF table for ammonia, ref 1 or 6) gives

$$\mu^0_{NH_3} = G^0_{NH_3} - H^0_{NH_3}(0) + \Delta H^0_{f,NH_3}(0) = -86.34$$
$$kJ/mol \tag{19}$$

As mentioned immediately after eq 7, the zero kelvin enthalpy and Gibbs free energy are the same. The same identity applies to the heat of formation where

$$\Delta H^0_{f,i}(0) = \Delta G^0_{f,i}(0) \tag{20}$$

This can be confirmed by examining the $T/K = 0$ entry for both of these values in the ammonia table (columns 6 and 7) and recognizing that the numerical values are identical. Hence eq 19 can be written

$$\mu^0_{NH_3} = G^0_{NH_3} - G^0_{NH_3}(0) + \Delta G^0_{f,NH_3}(0) = -86.34$$
$$kJ/mol \tag{21}$$

which is appealing since in eq 21 only the Gibbs free energy is used to express $\mu^0_{NH_3}$.

With these three standard chemical potentials, the standard Gibbs free energy for the production of 2 mol of ammonia at 298.15 K can be determined to be -32.73 kJ. If the reference temperature (298.15 K) had been used instead of 0 K for the determination of the standard potentials, three new values of $\mu^0(T)$ would be determined, but, obviously, the Gibbs free energy change for the reaction would remain the same. In Table 1, the set of $G^0 - H^0(T)$ calculated referenced to 0 K and

Table 1. Standard Chemical Potential Values Referenced to the Enthalpy at 0 and 298.15 K

	$\mu^0 = G^0 - H^0(T_r)$ @ 298.15 K (kJ/mol)	
molecule	$T_r = 0$ K	$T_r = 298.15$ K
NH_3	-86.34	-103.36
H_2	-30.50	-38.96
N_2	-48.46	-57.12

referenced to the reference temperature of the table are displayed along with the change in the Gibbs free energy associated with the reaction shown in eq 9. The data displayed in Table 1 illustrate the point made at the beginning of this presentation that the numerical value of a chemical potential is based upon a convention. The two different conventions used in Table 1 are the two different enthalpy reference temperatures, T_r. Yet, as must be the case, the value of ΔG^0 for a given chemical equilibrium is unaffected by the choice of convention, and in this case equals -32.72 kJ.

Calculation of the Molecular Partition Functions

In addition to using the JANAF tables for determining numerical values of the standard chemical potentials, the tables can be used for determining numerical values for molecular partition functions. Students find this particularly helpful given the nuances involved in calculating partition functions directly. As an example, consider the equilibrium

$$H_2(g) + I_2(g) \rightleftarrows 2HI(g) \tag{22}$$

Knowledge of the numerical values of the partition functions for H_2, I_2, and HI can lead to a determination to the numerical value of the equilibrium constant (ref 3, p 1068),

$$K(T) = \frac{q_{HI}^2}{q_{H_2} q_{I_2}} \tag{23}$$

The connection between the standard chemical potential and the partition function, q^0, can be seen in eq 2, which can be rewritten (ref 3, p 947)

$$\mu^0(T) = -RT \ln\left[\left(\frac{2\pi m k T}{h^2}\right)^{3/2} \frac{kT}{P^0}\right] = -RT \ln\left[\frac{q^0}{V} \frac{kT}{P^0}\right] \tag{24}$$

The partition function is written as q^0 to emphasize that, like $\mu^0(T)$, the zero of energy is the ground state of the atom or molecule in question. Such a zero of energy is not convenient when using eq 23 because the molecules in this case have different ground states. For eq 23 a more appropriate zero of energy is the separated atoms. The partition function for this zero of energy is designated q as in eq 23. The relationship between these two zeros of energy and the corresponding

partition functions is shown in Figure 2. The q^0 values can be determined from the JANAF tables using eq 25 which follows immediately from eq 24,

$$\frac{q^0(T)}{V}\frac{RT}{N_A P^0} = e^{-\mu^0(T)/RT}$$

(25)

where N_A is Avogadro's number. The exponent in eq 25 can be determined as was previously done using eqs 11−13.

The conversion of a JANAF table partition function, q^0, to one based on a separated atoms zero of energy, q, is shown in eq 26 (ref 3, p 948),

$$q_i = q_i^0 e^{D_{0,i}}$$

(26)

where D_0 is the energy difference between the ground state of the molecule in question and the separated atoms (Figure 2).
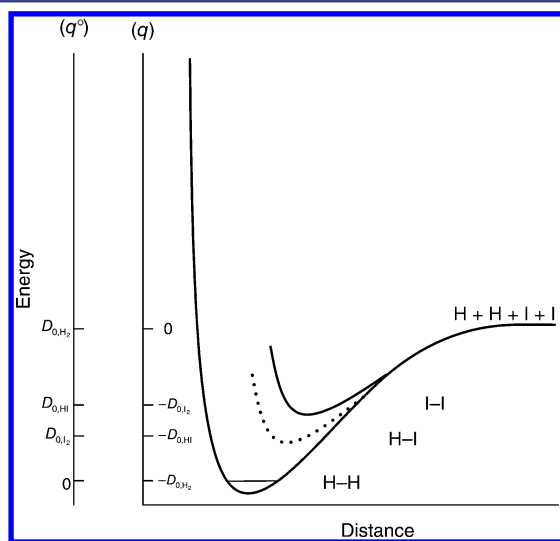

Figure 2. Separated atoms (q) versus molecular ground state (q^0) used for the (arbitrary) zero of energy when calculating partition functions. The importance of a single zero is illustrated. For the $H_2(g) + I_2(g) \rightleftarrows 2HI(g)$ equilibrium, the logical molecular ground state for zero is $H_2(g)$.

In the case of atomic partition functions, $q_i = q_i^0$. When eq 26 is substituted into eq 23, the result for this example calculation becomes

$$K(T) = \frac{(q_{HI}^0)^2}{(q_{H_2}^0)(q_{I_2}^0)} e^{(2D_{0,HI} - D_{0,H_2} - D_{0,I_2})/RT}$$

(27)

The D_0 values are included in JANAF tables for some molecular elements and can be calculated for molecular elements and compounds. For example, in the case of HI, D_0 equals the appropriate combination of the enthalpies of formation at 0 K of HI(g), I(g), and H(g), all to be found in the JANAF tables.

Calculating the q_i^0 at 298.15 K proceeds as follows using HI as an illustration. Column 4 at 298.15 K gives

$$-[G^0 - H^0(T_r)]/T = 206.589 \quad J/(\text{mol·K})$$

(28)

and column 5 at 0 K divided by 298.15 K gives

$$H0 - H(T_r)/298.25 = -8,656/298.15 = -29.032$$

$$J/\text{mol·K}$$

(29)

These combine to give

$$-(G^0 - H_0^0)/298.15 = 177.557 \quad J/\text{mol·K}$$

(30)

which when substituted into eq 25 for $-\mu^0(T)/T$ results in

$$\frac{q_{HI}^0}{V} = 4.569 \times 10^{34} \quad \text{m}^{-3}$$

(31)

The remaining numbers needed to complete the calculation of $K(298.15)$ are given in Table 2.

Table 2. Partition Functions and D_0 Values

molecule	q^0/V (m^{-3})	D_0 (kJ/mol)
H_2	5.346×10^{30}	432.071
I_2	1.697×10^{37}	148.816
HI	4.569×10^{34}	294.664

The final result for $K(298.15)$ is 692. This can be compared to the $K(298.15)$ determined from

$$\Delta G^0 = -RT \ln K(T)$$

(32)

and

$$\Delta G^0 = \Delta G_{f,\text{products}}^0 - \Delta G_{f,\text{reactants}}^0$$

(33)

where the Gibbs free energy of formation of the species involved are listed in column 7 of the JANAF table. This calculation gives a value of $K(298.15) = 690$. When ΔG^0 is calculated using eq 10 and the methods that follow it for calculating $\mu^0(T)$, $K(298.15) = 691$.

Most of the calculations presented in this article have been done for 298.15 K. However, another benefit of introducing students to the JANAF tables is that the data in the tables cover a wide range of temperatures. All of the calculations presented here could just have easily been performed at a different temperature. This allows a direct examination of how the numerical values of quantities such as the standard Gibbs free energy, the enthalpy of reaction, or partition functions change over a wide range of temperatures.

■ PEDAGOGY

The material described in this paper is presented in a physical chemistry lecture course which focuses on thermodynamics. Students enrolled in the course are typically third year chemistry majors. JANAF tables are presented throughout the course. Their use in the calculation of partition functions takes one 50 min lecture, and their use in equilibrium constants takes about half of a 50 min lecture. Problems are assigned for homework, and either the appropriate JANAF tables are provided as hardcopy or the link to online JANAF tables is provided.[6] Students generally are quite surprised to see the numerical agreement between a partition function calculated from molecular constants and the same partition function determined using thermodynamic data from the JANAF table.

■ SUMMARY

The introduction and use of the JANAF tables in undergraduate physical chemistry courses serves several purposes. First, it allows for a presentation of calculating numerical values, based on experimental thermochemical data, of the standard chemical potential. These calculations lead naturally to the conclusion that such calculations are relative and require a convention. A second purpose for introducing JANAF tables into undergraduate physical chemistry is that these tables

provide the necessary thermochemical data for determining numerical values of partition functions. The values of the partition functions determined from thermochemical data are not dependent on a model system such as the harmonic oscillator or the rigid rotor. The determination of partition functions using thermochemical data provides an important illustration of the link and the internal consistency between thermodynamics and quantum mechanics. The only drawback to using the JANAF tables is that their use is not self-evident and requires some practice on the part of the practitioners.

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Notes

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